

HIGHLY CONDUCTIVE, WATER INSOLUBLE AND THERMALLY STABLE PROTON EXCHANGE MEMBRANES FROM FUNCTIONALIZED POLYOXOMETALATES

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INDEPENDENT ASSESSMENT AND FINAL EISG REPORT

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ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

INDEPENDENT ASSESSMENT REPORT (IAR)

HIGHLY CONDUCTIVE, WATER INSOLUBLE & THERMALLY STABLE PEM FROM FUNCTIONALIZED POMS

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PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace. The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which 5% is allocated to the Energy Innovation Small Grant (EISG) Program. The EISG Program is administered by the San Diego State University Foundation through the California State University, which is under contract to the Commission.

The EISG Program conducts up to four solicitations a year and awards grants for promising proof-of-concept energy research.

PIER funding efforts are focused on the following seven RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Energy Innovations Small Grant Program
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally-Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies

The EISG Program Administrator is required by contract to generate and deliver to the Commission an Independent Assessment Report (IAR) on all completed grant projects. The purpose of the IAR is to provide a concise summary and independent assessment of the grant project in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions. The IAR is organized into the following sections:

- Introduction
- Objectives
- Outcomes (relative to objectives)
- Conclusions
- Recommendations
- Benefits to California
- Overall Technology Assessment
- Appendices
 - Appendix A: Final Report (under separate cover)
 - Appendix B: Awardee Rebuttal to Independent Assessment (awardee option)

For more information on the EISG Program or to download a copy of the IAR, please visit the EISG program page on the Commission's Web site at:

<http://www.energy.ca.gov/research/innovations>

or contact the EISG Program Administrator at (619) 594-1049, or email at:

eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at <http://www.energy.ca.gov/research/index.html>.

Highly Conductive, Water Insoluble & Thermally Stable PEM from Functionalized POMS

EISG Grant # 00-15

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Grant Term:	February 2001 – January 2002

Introduction

Proton exchange membrane (PEM) fuel cells could play an important role in future distributed electricity generation in California. Operating in a combined heat and power mode they could provide very high total fuel efficiency (~80%), essentially zero emissions, and highly reliable power. At this time the cost of the membrane in the PEM fuel cell is keeping this type of fuel cell expensive. In addition current PEM fuel cells do not display the required reliability and lifespan for long-term high temperature applications. Shortcomings in the membrane material are believed to be the cause of the limited reliability and lifespan. If these could be overcome, the PEM fuel cell could be widely installed in grid-connected applications.

Overall fuel utilization for the state could move higher than the current ~30% if PEM fuel cells were installed in small heat and power applications. Emissions of CO₂, NO_x, and even SO_x would decrease as the use of the PEM fuel cell increased. The cost of electricity and thermal energy should decrease at the same time. The researcher established a goal of reducing the cost of the membrane to \$2 per square meter from the current value of \$500 to \$1000 per square meter.

For effective stationary power generation PEM fuel cells should be designed to run at operating temperatures between 120 and 140°C. High temperature operation reduces the impact of carbon monoxide poisoning in reformat air-fuel cells, and allows attainment of high power density. Success in developing thermally stable, conducting materials for membranes could have a tremendous impact on achieving high temperature operation. By eliminating the hydrous component, it is anticipated that water re-circulation hardware will not be necessary and thermal management issues will be relieved, thus greatly simplifying the overall fuel cell system.

The goal of this project was to prove the feasibility of using a highly conductive (proton) and thermally stable inorganic electrolyte for proton exchange membrane fuel cell (PEMFC) based on functionalized polyoxometalates (POM) membranes. Polyoxometalate has been proven to have high temperature proton conductivity (0.17 S/cm) and much lower cost than Nafion. Nafion is the membrane material most often used in PEM fuel cells. The main drawbacks of POM are poor film forming capability, and high solubility in water. Its conductivity is also sensitive to humidity and temperature. The researcher planned to use functionalized POM inorganic polymers to produce membranes with: (1) membrane forming capability, (2) improved ionic

conductivity, and (3) thermal stability. The researcher hypothesized that no water management system would be required to achieve high proton conductivity.

Objectives

The goal of this project was to determine the feasibility of developing a polymer membrane based on POM material for PEM fuel cell that is highly proton conductive, water insoluble and stable across a wide temperature range. The researcher established the following project objectives:

1. Develop a POM membrane that is thermally stable in the temperature range of 25 to 140 deg C.
2. Develop a POM membrane with proton conductivity of 0.01 - 0.10 S/cm.
3. Develop a POM membrane that is water insoluble.
4. Reduce the cost of PEM membranes to less than \$2 per square meter from the current \$500 to \$800 per square meter.

Outcomes

1. The researcher functionalized a POM monomer forming an inorganic polymeric structure, in which POM anion unites were connected through bridge ligands, bearing protons and hydrates in its network structure. The hybrid membrane electrolyte coatings demonstrated stable operation up to 150°C, but with a partial loss of water content.
2. At 100° C, the researcher found that the conductivity ranged from 0.01 to 0.1 S/cm when the relative humidity ranged from 60 to 100%.
3. The materials selected by the researcher were insoluble in water.
4. The researcher presented only raw material costs to satisfy this objective. Actual membrane cost was not determined.

Conclusions

1. The researcher developed membranes that are stable to 150° C. However, the increase in cell resistance as temperature is increased indicates that the cell is drying out causing the membrane's conductivity to decrease. This is not a good sign for a membrane that is supposed to operate above 100° C. Cell resistance was not measured above 80° C.
2. Conductivity should be compared to Nafion, the commonly used membrane material. A conductivity change of over an order of magnitude for a relative humidity change of 60% is very dependent on water content. The claim is made that this is less sensitive than phosphotungstic (PWA) solid acid membranes, but data is not shown by the researcher to allow the comparison
3. The researcher satisfied this objective.
4. The researcher has not progressed to a point where a credible manufacturing cost can be established. If the membrane material were to be incorporated into a PEM fuel cell the cost of the fuel cell should decrease markedly.

This project did not present sufficient data to prove the feasibility of using polyoxometalate hybrid membrane electrolyte assembly (MEA) in high temperature (150° C) PEM fuel cell applications.

Recommendations

This project, while not proving the feasibility of POM material for PEM fuel cell membranes did advance the science of this concept and provides encouragement that this concept is sound. Additional research should be accomplished to meet the objectives of this project before committing funds to a field test. The Program Administrator recommends that the researcher firmly establish the performance of the material at 150° C. New laboratory tests should confirm electrochemical stability and investigate the strong dependence of the conductivity on relative humidity. The PA recommends that the researcher clearly compare material data for the functionalized POM with the published properties of Nafion, the most widely used membrane material for PEM fuel cells.

Benefits to California

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impact of the California electricity supply. PEM fuel cells could find wide acceptance in grid-connected distributed generation if the price of the fuel cell were reduced and its reliability were increased. Once proven feasible, the functionalized POM material developed in this project may provide these benefits. Until feasibility is fully proven however, it serves no purpose to speculate further.

The research conducted in this project could lead to increased reliability of PEM fuel cells especially when operated at high temperatures. The benefits to ratepayers cannot be determined at this time since the membrane material cost has not been adequately characterized, nor has the reduced cost of the membrane been factored into the cost of a PEM fuel cell system.

Overall Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researcher's overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researcher has identified the market for the functionalized POM material. Distributed generation with combined heat and power is the prime market opportunity for the material under development. This is an important market segment for California. The researcher should discuss market needs with companies developing PEM fuel cells for stationary applications.

Engineering/Technical

Early discussions with a fuel cell developer could provide the researcher with the requirements for a commercial membrane. In addition, the researcher must scale-up the manufacturing process for polyaluminatic solid acid material. With current technology, the researcher was able only to make batches of <1kg. Material cost is highly dependent on the processes employed to produce large quantities of the material.

Legal/Contractual

The researcher has provided no evidence of a patent application.

Environmental, Safety, Risk Assessments/ Quality Plans

Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental. The researcher should begin the development of manufacturability plans and product cost studies. Other studies can be delayed until the concept is fully proven.

Production Readiness/Commercialization

It is premature to consider production readiness of this membrane. However, the researcher should begin discussions with PEM fuel cell developers to assure that the proposed membrane meets all of the product specifications.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

EISG FINAL REPORT

HIGHLY CONDUCTIVE, WATER INSOLUBLE & THERMALLY STABLE PEM FROM FUNCTIONALIZED POMS

EISG AWARDEE

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program. The EISG Program awards grants up to \$75,000 for promising public interest energy research that is in the proof-of-concept stage of development.

PIER funding efforts are focused on the following six RD&D program areas:

- Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

For more information on the EISG Program, please visit the Commission's Web site at:
<http://www.energy.ca.gov/research/innovations>

For more information on the overall PIER Program, please visit the Commission's Web site at:
<http://www.energy.ca.gov/research/pier>

Inquires related to this final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619) 594-1049.

Executive Summary

The proposed research is to develop highly proton conductive and thermally stable inorganic electrolyte for proton exchange membrane fuel cell (PEMFC) based on functionalized POM membrane. POM has been proven to have high temperature proton conductivity (0.17S/cm) and much lower cost than Nafion. Main drawback of POM is poor film forming capability and high solubility in water. Its conductivity is also sensitive to humidity and temperature. Functionalized POM inorganic polymeric network (1) will provide POM with membrane forming capability.(2) the ionic conductivity will be further improved, because anions are integrated into network backbone and thus immobilized; protons are the only movable ions in the polymeric system

The specific objectives of the program are:

- Functionalization and polymerization of PWA with different cross-linking agents.
- Characterize the chemical and physical properties of functionalized PWA as a function of reaction conditions.
- Investigate the film forming ability of the TiSiPWA hybrid.
- Evaluate the chemical and physical properties (ionic conductivity, chemical stability, thermal stability, humidity influence, gas permeability, etc.) of the film in a single cell (tested at FuelCell Energy).

All the objectives have been successfully accomplished. The proof of feasibility of using polyoxometalate (POM) hybrid membrane-electrolyte assembly (MEA) as high temperature (150°C) proton exchange fuel cell (PEMFC) applications has been firmly established. Furthermore, the testing results show that its superior high temperature proton conductivity and electrochemical stability over Nafion and other solid electrolytes. This is a key milestone in developing a low-cost, easy-to-manufacturing MEAs for high temperature PEMFC. Due to the successful completion of the research, a solid foundation has been prepared for the next phase.

The efforts recommended include: 1). Further development of high protonic conductive hybrid solid electrolyte by optimization of composition and process parameters; 2) Incorporation of hybrid POM/sol-gel into the cathode to promote intimate contact among Pt, the protonic species and the reactants for high cathode voltage generation; 3) Further development and scaling up of MEAs fabrication technology; 4).Study/testing the MEAs in single fuel cell and optimize the performance of the MEAs.

After successful completion of next phase, the process will be ready for use in commercial stacks.

Abstract

The proposed research is to develop highly proton conductive and thermally stable inorganic electrolyte for proton exchange membrane fuel cell (PEMFC) based on functionalized POM membrane. POM has been proven to have high temperature proton conductivity (0.17 S/cm) and much lower cost than Nafion. Main drawback of POM is poor film forming capability and high solubility in water. Its conductivity is also sensitive to humidity and temperature. Functionalized POM inorganic polymeric network (1) will provide POM with membrane forming capability. (2) the ionic conductivity will be further improved, because anions are integrated into network backbone and thus immobilized; protons are the only movable ions in the polymeric system. The conductivity will be competitive with state-of-art PEMs. (3) hydrates form hydrogen bond with bridge ligand and polymeric network, therefore hydrates can be stabilized and protected to higher temperature. No water management system is needed to achieve high proton conductivity.

I. Introduction

1.1 Introduction

The proposed research is to develop highly proton conductive, water insoluble and thermally stable electrolytes for proton exchange membrane fuel cell (PEMFC) based on functionalized polyoxometalates (POM) polymer membrane. Polyoxometalate has been proven to be highly proton-conducting at room temperature [1] and cost-effective[2]. Main drawback of POM is poor film forming capability and high solubility in water. Its conductivity is also sensitive to humidity and temperature. Functionalized POM polymers will be water insoluble, less sensitive to humidity and temperature, and having good film formability and proton conductivity.

Proton Exchange Membrane Fuel cells provides efficient and free of emissions (SO_x and NO_x) power. They offer the best alternative to conventional power generation technologies for a variety of applications. For fuel cells to be commercially competitive, issues such as cost, size, and functionality need to be addressed. Although research efforts so far have advanced PEMFC technology significantly, substantial improvements beyond the current state-of-the-art are required before commercialization can be achieved. In particular, PEM needs to be improved. The objective of this proposal is to demonstrate the feasibility of producing low-cost, easy-to-manufacture PEM with functionalized polyoxometalates. This process promises a cost-effective, electrolyte membrane that has high proton conductivity both at room temperature and higher temperature and is less sensitive to humidity change.

Polyoxometalates (POM) have long been exploited for their solid-state ionic conductivity.[3] Among the various polyoxometalates, phosphotungstic acid (PWA) and phosphomolybdic acid (PMA) in their 30-water molecule hydrate forms (H₃PW₁₂O₄₀·30H₂O and H₃PMo₁₂O₄₀·30H₂O, respectively) are characterized by considerable protonic conductivity, due to the proton hopping in the hydrogenbonded networks facilitated by hydrate molecules.[4] More specifically, solid state, room temperature PWA has a protonic conductivity of about 0.17 S/cm, and PMA, also at room temperature, has a protonic conductivity of about 0.18 S/cm. Table 1 shows the comparison of conductivity between POM and different kinds of perfluorocarbon ion exchange polymers.[5] The compression molded POM plates were demonstrated to function effectively as partition walls between the anode and cathode chambers of H₂ (catalyst Pt or Pd)/O₂ fuel cells. According to a Japanese patent by Nakamura, a cell built with POM plate as electrolyte operated at room temperature by using an electrode surface area of 0.385 generated a voltage of 2V.[4] Additionally, POM is a low cost material (\$2.0/ m²), compared to Nafion membrane (\$500-1,000/m²).

One major limitation of the POM materials is its poor film forming capability and high solubility in water. Instead of forming a membrane to be used as electrolyte, the POM materials have to be pressed into a plate, resulting in excessive electrolyte thickness. The high pressures were also needed to eliminate any microfine porosity from the plate. The excessive thickness caused the diffusional problems and high ionic resistance. Another limitation of POM is its sensitivity to relative humidity and temperature, due to its high degree of hydration. Therefore, it is highly desirable to

develop an approach to improve POM's operating temperature range and film forming capability, meanwhile retain its high proton conductivity.

Table 1. Ionic conductivity of PWA, PMA and perfluorocarbon ion exchange polymers

Materials	Proton Conductivity (S/cm)	Cost
PWA	0.17	\$2.0/m ²
PMA	0.18	--
Dow	0.114	--
Aciplex-S	0.108	--
Nafion-115	0.059	\$500-1,000/m ²

In this proposal, POM monomer will be functionalized to form inorganic polymeric structure, in which POM anion units are connected through bridge ligands, bearing protons and hydrates in its network structure. Several outstanding effects are expected from this functionalization. (1) interconnected polymeric structure will provide POM with membrane forming capability. (2) the ionic conductivity will be further improved, because anions are integrated into network backbone and thus immobilized; protons are the only movable ions in the polymeric system. The conductivity will be competitive with state-of-art PEMs. (3) hydrates form hydrogen bond with bridge ligand and polymeric network, therefore hydrates can be stabilized and protected to higher temperature. No water management system is needed to achieve high proton conductivity.

High conductivity at higher temperature will eliminate water recirculation hardware or pressurization operation, greatly simplifying the overall fuel cell system. In addition, the cell could be operated at elevated temperatures (in comparison to PEM FCs) which would yield more tolerant electrodes to reaction poisons such as CO from reformat fuel.

1.2 Technical background

For PEM application, low temperature and high temperature operations are both desirable, because they allow a variety of operating conditions to be used. Low temperature electrolytes, in the range of 25 to 60 °C, are suitable for portable fuel cells. High temperature electrolyte, from 120 to 140 °C, is desirable for high power larger fuel cells. High temperature fuel cell also reduces the impact of carbon monoxide poisoning in reformat air fuel cells and allows attainment of high power density. All fuel cells will be started up at low temperature in order to reach the high temperature. Therefore, low

temperature stability is important for either application. In addition to fuel cell application, these solid electrolytes can be used for supercapacitors, electrochromic devices, sensors, etc.

There are two types of low temperature proton conductors (<150 °C). One is polymer based, such as Nafion, whose proton conductivity is high, almost comparable to aqueous HCl and liquid H₃PO₄, but it needs water management to keep it hydrated and is only utilizable up to around 100°C, where it starts to dehydrate and desulfonate. Another type is inorganic proton conductors, such as CsHSO₄, 12-WPA, β"- alumina, and various zirconium phosphate hydrates, which represent a system with crystallographic protons. Most of these inorganic proton conductors have very low room temperature conductivity. For example, CsHSO₄ has a conductivity of less than 10⁻⁶ S/cm at room temperature; it will become a fast proton conductor around 140°C with a conductivity in between 10⁻³ ~10⁻² S/cm. Another intrinsic problem with inorganic proton conductors is their poor membrane forming capability. Currently, there is no proton conductor that can work effectively from room temperature to 150 °C.

Phosphotungstic acid (PWA) and phosphomolybdic acid (PMA) in their 30-water molecule hydrate forms (H₃PW₁₂O₄₀.30H₂O and H₃PMo₁₂O₄₀.30H₂O, respectively) are characterized by considerable protonic conductivity (0.17 S/cm and 0.18 S/cm, respectively), due to the proton hopping in the hydrogenbonded networks facilitated by hydrate molecules.[6] Their sensitivity to humidity and temperature made them less attractive for applications. Therefore, efforts are made to synthesize POM compounds with sufficiently high conductivity, but less sensitive to the changes of temperature and relative humidity.

1.2.1 WPA incorporated in silica gel.

Since WPA has very high room temperature proton conductivity, extensive efforts have been put to make WPA less sensitive to humidity and working temperature. The sol-gel process is a promising way for obtaining materials with new characteristics used for solid state ionic by increasing the stability and conductivity of various inorganic material in gel matrices.

Different amount of WPA (from 8.5 to 73.1 mass%, which correspond to 0.5 to 4.7 mol%) has been incorporated in silica gel. The doped gel powder was pressed to a tablet under a pressure of 2.9x10⁸ N/ m² for analysis. IR spectra indicated that a larger quantity of water was retained on doped silica than on pure silica and WPA itself. Different protonic entities (OH groups, water molecules and oxonium ions), bonded with hydrogen bonds of different strengths, are present in gels. This network of hydrogen bonds enables fast proton transport through the matrix. Conductivity measurements show an increase in WPA stability when incorporated in silica. At room temperature, pure WPA.6H₂O has a conductivity of 3.0x10⁻¹¹ S/cm. After being doped in silica gel at a 3.3 mol% concentration, the conductivity reaches 0.01S /cm, which is nine orders higher than that of pure 6-WPA and two orders higher than silica gel (1.3x10⁻⁴ S/cm).

Thermal stability of doped WPA was also improved due to the protection provided by silica gel matrix. Hydrates are able to form hydrogen bond with bridge

ligand to be further stabilized. Silica gel contains water molecules in macro, meso, and micropores, which are retained in the matrix up to 180°C. Silanol groups (Si-OH) will be able to stand much higher temperatures (~500°C). These enhanced water uptake properties of the silica gel will help to increase the working temperature range of WPA.

WPA doped silica gel has shown many promising properties as proton conductors. However, there are several disadvantages associated with this approach:

- a. Limited WPA doping concentration. The conductivity of doped gel is directly proportional to WPA concentrations. With current approach, only 3 mol% WPA can be incorporated into silica gel, otherwise it will cause phase separation and WPA can not be fully protected.
- b. Poor film forming capability. With high loading of WPA, the doped gel is obtained in powder form instead of a film.
- c. Not a single ion conductor. WPA is simply incorporated in the gel matrix; anions are not stabilized in the structure. By reducing the mobility of anions, the conductivity will be further improved.

1.2.2 Polyoxometalates and its functionalization

WPA belongs to Keggin-type (Fig.1) heteropolyanion metalates.[7] They have some unique properties, such as proton transfer/storage abilities, ionic conductivity, thermal stability, and very weak interaction with the cations. One important development of organometallic chemistry of POMs is the functionalization of POM through cross-linking agent, so that they can form polymeric network. In principal, this process can be achieved either by reaction between preformed macromolecules and a cross-linking agent or by copolymerization of a classical monomer and a cross-linker. The functionalization of POM by polymerizable double bonds has been shown to be effective.[8]



Fig. 1 The Keggin structure, shared by $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ and many other heteropolyanions.

Most functionalization work was focus on “unsaturated” Keggin-type anions, such as $[\text{SiW}_{11}\text{O}_{39}]^{8-}$, $[\text{PW}_{11}\text{O}_{39}]^{7-}$, etc., which are normally available as polyanion salts. They can easily react with common silanes. Cedric R. Mayer and Rene Thouvenot[9] demonstrated $[\text{SiW}_{11}\text{O}_{39}]^{8-}$, could be functionalized by $\text{RSi}(\text{OR}')_3$ in water, where R was

$\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{O})\text{OPr}$ (Fig.3). $[\text{SiW}_{10}\text{O}_{36}(\text{RSi})_2\text{O}]^{4-}$, the functionalized $[\text{SiW}_{11}\text{O}_{39}]^{8-}$, was further copolymerized with ethyl methacrylate in CH_3CN to form a network. Sol-gel transitions were observed during the reaction at different times depending on the reactant ratio. The polymer can be used as elastomer.

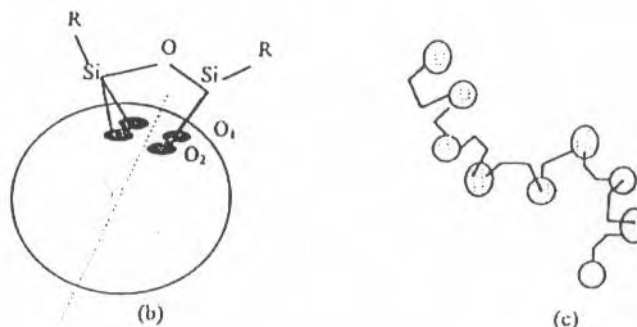


Fig. 2. Representation of the functionalized polyanion $[\text{SiW}_{11}\text{O}_{39}(\text{RSi})_2\text{O}]^{4-}$ and the networks.

Keggin fragments, including $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$, which are readily available in polyacid form, can be functionalized in a similar manner to that of “unsaturated” Keggin-type anions. The only difference is that the cross-linking agents engaged are normally Ti based, such as RTiCl_3 . [8]

To achieve high conductivity in functionalized POMs, it is critical to maintain the structural integrity of POM after the functionalization. According to the IR and NMR analysis data for the polyanion in the gel, [10] it was found that the structural integrity of the polyoxotungstate moiety has been preserved. It is therefore expected that the intrinsic properties of the polyanion engaged in the cross-linking knots should express though the gel. D. Griller⁷ has confirmed that functionalized $[\text{SiW}_{11}\text{O}_{39}(\text{RSi})_2\text{O}]^{4-}$, when recrystallized from water as teteamethylammonium salts, retained its hydrates. It was also found that the mobility of the polyanion units in the gel was reduced.

1.2.3 The uniqueness of proton conducting POM polymer

There is a need to develop a low-cost, easy-to-manufacture PEM material with high ionic conductivity, power density, and thermal stability, as are essential for the success of fuel cell applications. The synthesis and application of this functionalized POM material as proton conductor is an unprecedented work, to our knowledge. The following are the unique features for this kind of materials:

1. **Crosslinked networks.** Polyanions are integrated and immobilized in the silica networks, bearing hydrogen ions and hydrates in its structure. It can be fabricated to dimensional membrane. Polymeric SiPOM has showed good mechanical properties. It can be used as elastomer.
2. **Single ion conductor.** The polyanions are part of the network backbone. Therefore, it is naturally immobilized and proton is the only mobile cation, as could significantly increase proton transference number.

3. **High WPA loading.** Functionalized WPA will form the backbone of the polymeric structure, therefore, its concentration can be very high without causing any phase separation. High conductivity can be achieved.
4. **Weak cation-anion interaction.** It is well known that in polyoxometalate solutions, the cation-anion interactions are weaker than most of the conventional metal salts in solution. This is because the delocalization of the anion charge (-2 or -3) over the entire cluster weakens the charged cation-anion interaction, as leads to an increased proton mobility.
5. **Low cost.** PWA only costs approximately \$2/m², compared to Nafion membrane priced at \$800/m². Titanium and silicon oligomers will be inexpensive if synthesized in large quantity.
6. **High thermal stability and wide working temperature range.** Functionalized PWAs are more thermally stable. They are expected to have reasonable high ion conductivity up to 140°C, as enables PEM fuel cells to be operated at higher temperatures, leading to enhanced catalyst performance, CO tolerance, and efficiency.
7. **Water insoluble.** The polyoxometalate polymer does not dissolve in water. This is a drawback of most of the other electrolyte materials. Therefore, the proposed solid electrolyte can be used in 'wet' environment as well.
8. **Elimination of water hydration system.** The high solid-state ionic conductivity of PWA is due to intrinsic hydrogen bonded networks facilitated by hydrate molecules. Therefore, it eliminates the need for costly internal water hydration system that is needed for the traditional polymer membranes, thus, greatly simplifying the overall fuel cell system and further reducing the cost.
9. **Hydrogen bond with bridge ligand to further stabilize the hydrates.** Stabilization of hydrates are essential for this application, because of mechanism of proton conduction of functionalized POM polymer.

1.3 Summary

Functionalized PWA materials will have (1) good film forming capability, (2) high proton conductivity, room temperature conductivity competitive with state-of-art PEMs, but with no water management system, (3) extended working temperature range, due to the protection provide by the network structure and enhanced water uptake properties of the network.

Developments of the proposed proton conducting materials will have immediate impact on a wide range of commercial power sources from computer power to emergency medical power supplies to recreational power uses.

1.4 Project Objectives

The overall objective of the proposal is to demonstrate highly conductive PEM membrane can be obtained from functionalized POM networks and to investigate the properties of the materials synthesized by this process. The specific objectives of the program can be enumerated as follows:

- Functionalization and polymerization of PWA with different cross-linking agents.

- Characterize the chemical and physical properties of functionalized PWA as a function of reaction conditions.
- Investigate the film forming ability of the TiSiPWA hybrid.
- Evaluate the chemical and physical properties (ionic conductivity, chemical stability, thermal stability, humidity influence, gas permeability, etc.) of the film in a single cell (tested at FuelCell Energy).

II. Project Approach

We carried out the functionalization and polymerization of PWA in water solution to preserve the hydrates in the network structure. Specially synthesized, different water soluble titanium based oligomers, such as $(\text{RO})_2\text{R}'\text{Si-O-TiCl}_3$, will be used as cross-linking agent to functionalize PWA, meanwhile Si-OR functional group can be hydrolyzed and polymerized to form a network structure. Different cross-linking oligomers will be tested in this work. The beauty of this approach is that the structure of oligomers can be finely tuned to control the extent of polymerization and consequently the density of the film. In this way, we will obtain a strong and flexible TiSiPWA hybrid networks, bearing hydrogen ions and hydrates in its structure. Fig. 3 and 4 show the schematic structure of proposed PWA functionalized by $(\text{RO})_2\text{R}'\text{Si-O-TiCl}_3$ and thus obtained networks.

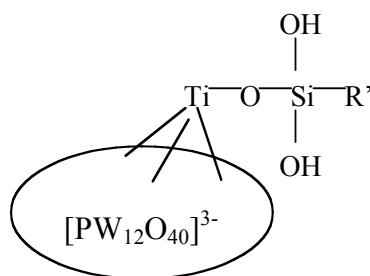


Fig. 3 Proposed structure of PWA functionalized by $(\text{RO})_2\text{R}'\text{Si-O-TiCl}_3$.

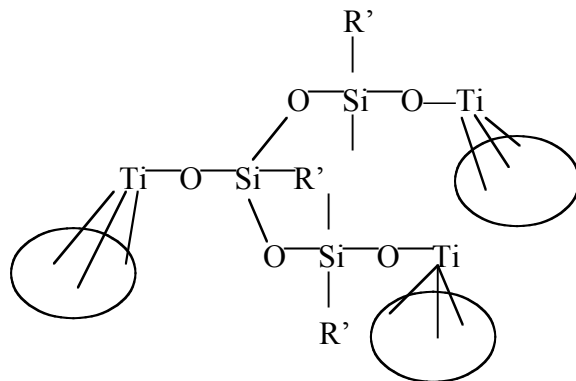


Fig. 4 Proposed structure of networks formed by the above functionalized PWA.

III. Project Outcomes

The overall goal of this SBIR goal is to demonstrate highly conductive PEM membrane can be obtained from functionalized POM networks and to investigate the properties of the materials synthesized by this process.

- (1) Functionalization and polymerization of PWA.
- (2) Characterization of functionalized PWA.
- (3) Investigate the film forming ability of TiSiPWA hybrid.
- (4) Evaluate the produced Proton Exchange Membrane.

All the task objectives have been successfully accomplished. These results strongly indicate that the proposed polyoxometalate (POM) hybrid membrane-electrolyte assembly (MEA) is feasible for high temperature (150°C) proton exchange fuel cell (PEMFC) applications and it showed superior high temperature proton conductivity and electrochemical stability over Nafion and other solid electrolytes. This is a key milestone in developing a low-cost, easy-to-manufacturing MEAs for high temperature PEMFC. Proton Exchange Membrane Fuel Cells yield power that is efficient and free of emissions (SO_x and NO_x). They offer the best alternative to conventional power generation technologies for a variety of applications. For fuel cells to be commercially competitive, issues such as cost, size, and functionality need to be addressed. Although research efforts so far have advanced PEMFC technology significantly, substantial improvements beyond the current state-of-the-art are required before commercialization can be achieved. In particular, the PEM and cathode need to be improved. This process developed in this research promises a cost-effective, electrolyte membrane which has high proton conductivity both at room temperature and higher temperatures, and which is less sensitive to humidity changes.

The research experiments, findings and results are described in detail below.

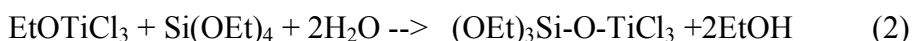
3.1. Ti-O-Si based oligomer preparation

Route a. From titanium butoxide and tetraethoxysilane

A titanium-silicon based oligomer is used as one type of cross-linking agent to functionalize polyoxometalate anion. The Ti/Si oligomer was synthesized by using titanium butoxide and tetraethoxysilane (TEOS) as starting precursors. Titanium butoxide and TEOS were dissolved in isopropanol with a mole ratio of 1:1. After stirring at room temperature for 5 hours, additional water was added. FTIR analysis showed formation of the Ti-O-Si bond (Fig. 4.1). Si-O-Si bond was also observed.

Route b. From titanium chloride and tetraethoxysilane

Titanium chloride and ethanol were mixed, with stirring, in a molar ratio of 1:1. TEOS and water were then added into the solution. The following reactions are assumed to proceed:



Then, the functionalization was accomplished by addition of $(\text{OEt})_3\text{Si-O-TiCl}_3$ to equivalent molar phosphotungstic acid which was dissolved in ethyl alcohol. The polymerization was then conducted by heating the solution in oven at 90C with the cap sealed.

3.2. Synthesis of Polyaluminatic cluster acid

There are only two polyoxometalates acid clusters commercially available: phosphotungstic acid and phosphomolybdic acid. Most previous research was based on these two clusters, and they yielded excellent room temperature proton conductivity of 0.17 S/cm. In this research, we developed a low valence heteroatom-based solid polyoxometalates acid cluster. It is clear that the clusters, such as $\text{H}_5\text{AlW}_{12}\text{O}_{40}$ and

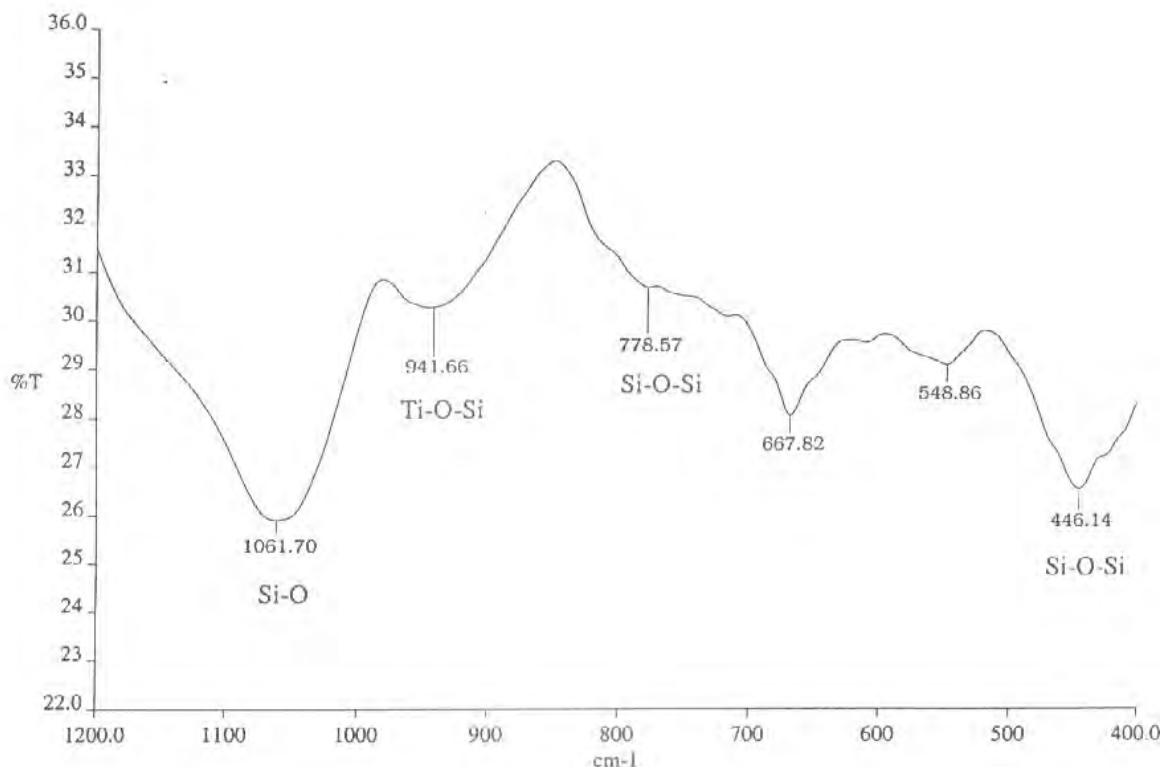


Fig. 5. FTIR spectrum of Ti/Si oligomer

$\text{H}_4\text{SiW}_{12}\text{O}_{40}$, are expected to have high conductivity, due to high proton loading levels. It is also known that these clusters are functionalized much more easily than the phosphotungstic acids or the phosphomolybdic acids.

We synthesized $\text{H}_5\text{AlW}_{12}\text{O}_{40}$ via two methods as shown in below.

a. Procedure 1

Dissolve Na_2WO_4 in H_2O and adjust pH level to 7.7 by adding HCl . Heat acid solution to reflux, and then add a solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ slowly over a 90 minute period. Solution was filtered through diatomaceous earth (Celite). Add H_2SO_4 into the solution to reach a pH of 0 and then add an additional 3mL of H_2SO_4 . Solution was heated at reflux for more than 7 days to complete the conversion. Allow it cool. Then add 500mL

of diethyl ether, and shake carefully. Let it settle; 3 layers should form and collect the bottom layer (heteropolyanion etherate). Repeat the shaking, venting, and collecting procedure until 3 layers no longer form. When extraction is near completion, the middle layer will appear less cloudy. Dry the combined etherate layers over a hot water bath.

b. Procedure 2

Combine 0.6 g of $\text{Al}(\text{OH})_3$, 16.7 g of WO_3 and 1.2 g of NaOH in 60 ml of water and place in autoclave. Apply 200 psi O_2 and heat for 6 hours at 200°C . Result is sodium salt, $\text{Na}_5\text{AlW}_{12}\text{O}_{40}$ in solution. Isolate the solid acid, $\text{H}_5\text{AlW}_{12}\text{O}_{40}$, by reaction of sodium salt with sulfuric acid, followed by ether extraction as described in Procedure 1, above.

The process should be carefully controlled in order to obtain the right compound. Small amounts of the solid acid, $\text{H}_5\text{AlW}_{12}\text{O}_{40}$, have been synthesized. Further development will be conducted in future research.

3.3. Hybrid materials synthesis

The overall objective is to make a POM based membrane with better film forming capabilities, while keeping its high proton conductivity. The bridge ligands selected for functionalization of the POM will have great effect on both proton conductivity and the mechanical properties of the resulting membrane. Proton conduction mechanisms can be also modified by the choice of bridge ligand used. For example, proton hopping in the hydrogenbonded network can be facilitated by hydrate molecular, ion motion coupled to the local motion of the polymer segments. This proton hopping along the ion coordinating sites can also play an important roles especially in higher temperature.

a. PWA/Ti-Si oligomer

Hybrid (1) was synthesized by mixing the PWA aqueous solution with $(\text{OEt})_3\text{Si-O-TiCl}_3$ oligomer at room temperature. By aging this mixture in a closed container, a yellowish gel can be formed. Coatings can be obtained from this solution.

b. PWA/Si hybrid

Dissolve PWA into water, and add TEOS, with stirring. Add IPA into the solution to enhance wetting ability of the solution to the substrate. The hybrid solution (2) was filtered before use.

The PWA cluster and hybrids were analyzed using FTIR analysis. The main vibrational bands of the hybrids are compared with Phosphotungstic acid (PWA) in Table 2. The shift of vibrational bands depend on anion-anion interactions and functionalization of the POM [10]. The $\nu\text{-W-O}$ mode exhibits a decreasing frequency when the anion-anion interaction weakened. The -Si-O-Ti-oligomer bridge ligand increases the length of the bridge ligand, and therefore weakens the anion-anion interaction.

Table 2. Comparison of the vibrational bands (cm^{-1}) appearing in the FTIR spectra.

Band assignment	PWA	PW/Si	PW/Si/Ti
ν -P-O	1080	1080	1089
ν -W-O	984	980	979
ν -inter W-O-W	891	900	898
ν -intra W-O-W	800	800	810
Si-O		1036	1045

c. $\text{H}_5\text{AlW}_{12}\text{O}_{40}/\text{Si}$ Hybrid

Dissolve 10g $\text{H}_5\text{AlW}_{12}\text{O}_{40}$ that prepared with the method described above in 20ml ethyl alcohol, and add 5g tetraethoxysilane and 0.2g polyethylene glycol under stirring.

3.4. Thermal Stability of Cluster Acid and hybrid

TGAs were performed to test the PWA and its hybrid's thermal stability. It was found that PWA stays stable at 150°C during a period of 3 hours. It also remains stable along a ramp up to 800°C, except that part of the crystalline water was lost. The commercially available PWA contains seven crystalline water based on the weight loss (Fig.6).

The aluminatic polyoxometalate solid acid shows that part of the crystalline hydrate can stable to very high temperature (~300°C), as shown in Fig.7. As we will discuss in the following sections, due to the combination of high proton loading and weakened interactions of proton to anion cluster, this solid acid exhibits much higher proton conductivities.

PWA/sol-gel hybrids exhibit three hydrate loss steps at temperatures of 60°C, 300°C and 430°C, as shown in Fig.8. The sol-gel hybrid did stabilize the crystalline water (from ~200°C to ~300°C). The 430°C water loss is probably due to dehydration from $\text{Si}(\text{OH})_4$ to SiO_2 .

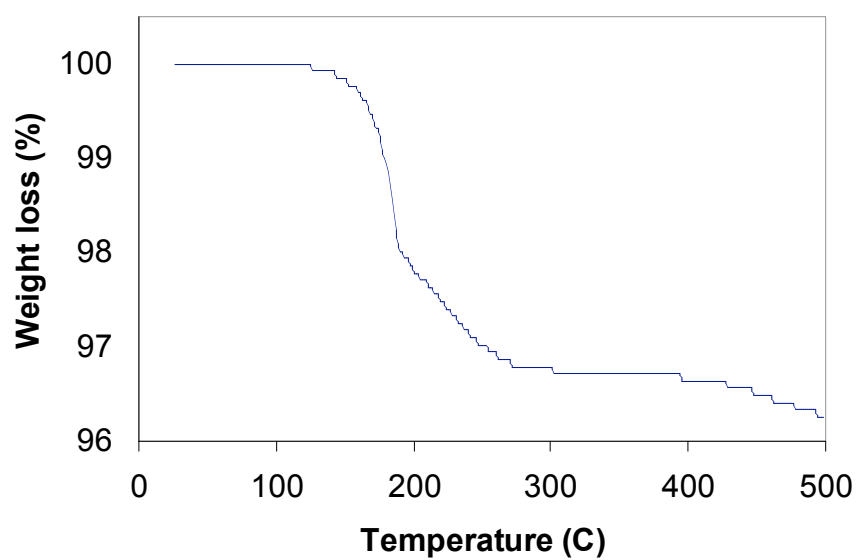


Fig. 6 TGA analysis for HWA.xH₂O, showing the high thermal stability of hydrates.

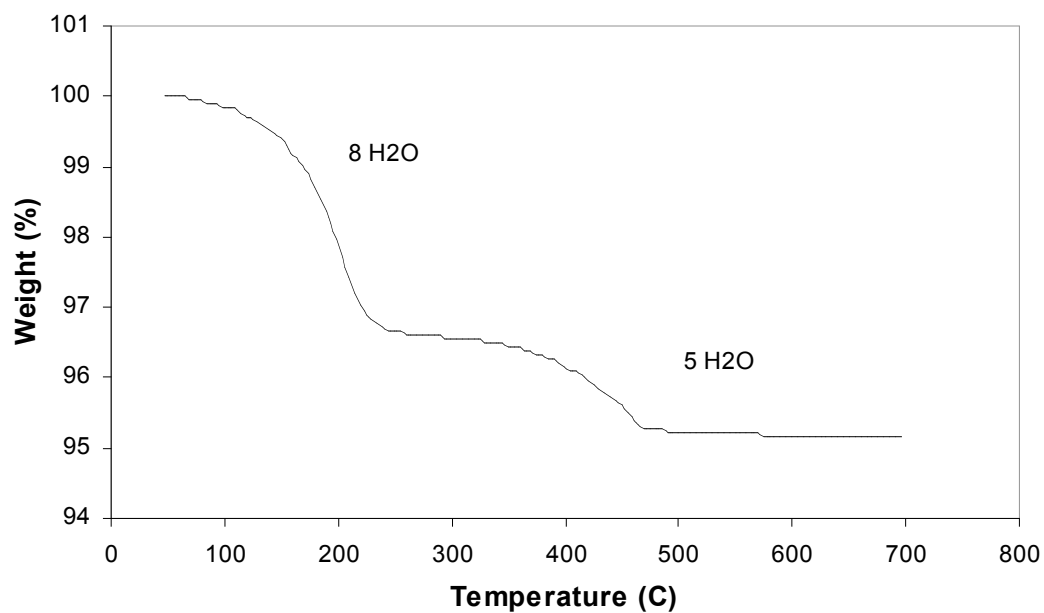


Fig. 7. Dehydrate of solid aluminatic acid as a function of the temperature.

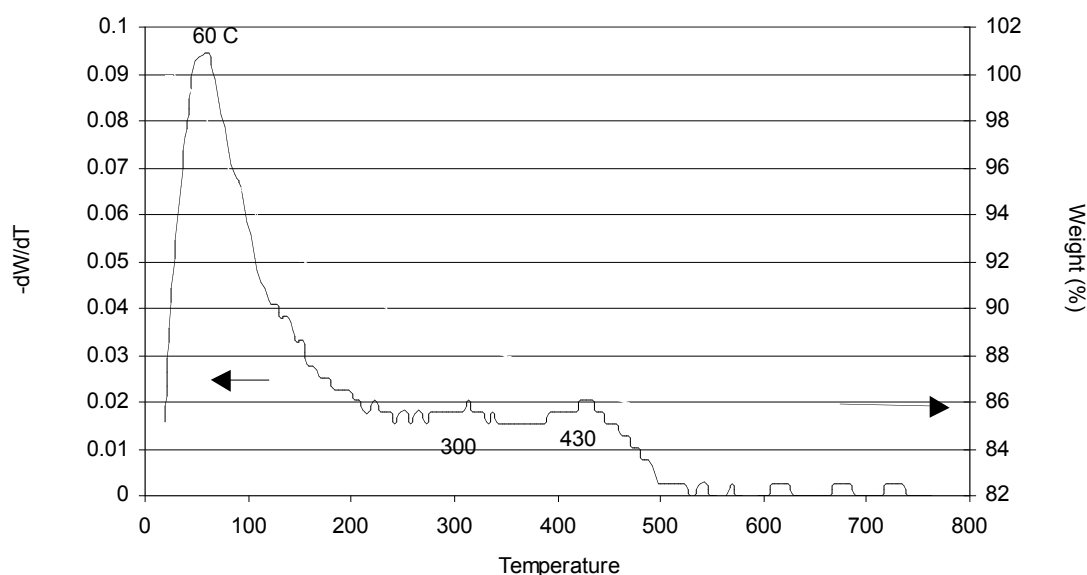


Fig. 8. Three hydrate loss step in PWA hybrid.

3.5 Membrane Film preparation

The main purpose of this research is to develop Membrane-Electrode Assembly, MEA. There are several possible approaches: 1) Synthesize the electrolyte membrane first and coat electrode composite on both sides of the membrane; 2) Coat electrolyte on top of carbon cloth supported cathode and anode, and assemble these two parts into fuel cell; 3) Coat electrolyte on top of the carbon cloth supported cathode and then coat anode on top of the electrolyte. In this research, we chose methods 2) and 3).

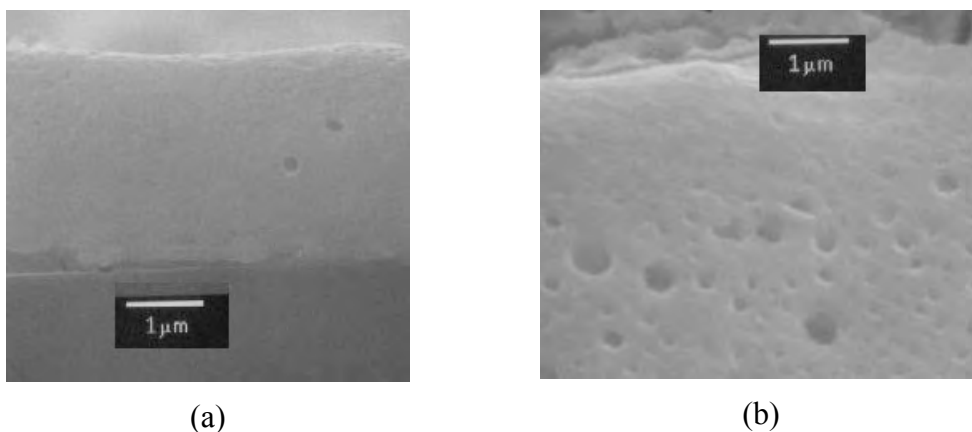


Fig.9. SEM microscopic photo on spin-on solid electrolyte coating.
(a) Cross section, (b) Surface of the coating.

The carbon cloth supported cathode was purchased from E-Tek. A glass substrate and a metal substrate were also used for testing. The electrolyte coating can be spin- or dip-coated. In this research, we use spin-coating due to the small size of the samples. The solution was applied onto substrate and spun at a speed of 2000 rpm for 30 seconds. The coating was cured on hot-plate at 180°C in air for various periods of time. The coating thickness depends on the concentration and viscosity of the solution. Aging of the hybrid solution resulted in viscosity increases. One layer coating can be 1 μm to 10 μm thick. Thicker one layer coatings tend to result a cracked film. The microstructure of a 3 micron thick coating is shown in Fig. 9.

3.6. Characterization of membrane coatings

The conductivity, gas permeability, and chemical and electrochemical stability of candidate membranes were evaluated. The flexibility of the membrane coating was tested. The polyoxometalate solid acid/sol-gel hybrids had excellent film formability, and were less moisture sensitive. The membrane coatings were very stable to temperature. The coating can be also applied to soft carbon cloth supported cathode sheet; the membrane-electrode assembly also displayed good processibility.

3.6.1. Flexibility

The membrane coating was spin coated on to titanium foil and cured at 180°C for 2 minutes in air. The coating was then bent to a 30-degree angle. These bent coatings were examined under the microscope. No cracks were observed.

3.6.2. Chemical and electrochemical stability

POM plates were demonstrated to function effectively as partition walls between the anode and cathode chambers of H_2 (catalyst Pt)/ O_2 fuel cells. A cell built with POM plate as electrolyte operated at room temperature using an electrode surface area of 0.385 generated a voltage of 2V. The POM and its hybrid are chemically and electrochemically stable.

3.6.3. Thermal stability

The hybrid membrane electrolyte coatings were very stable up to the temperature of 150°C, aside from a partial loss of water content. After heating a sample on a hot plate at 150°C for three days, no changes in conductivity, or physical changes, were observed.

Fig.10 shows the isothermal TGA of $\text{H}_5\text{AlW}_{12}\text{O}_{40}$ and its hybrid

3.6.4. Conductivity measurement

The conductivity was measured by using a simple four-point probe method, recommended by JPL researchers, that applied a constant current (1mA) while the voltage was measured. The measurement was conducted under different relative humidity and temperatures.

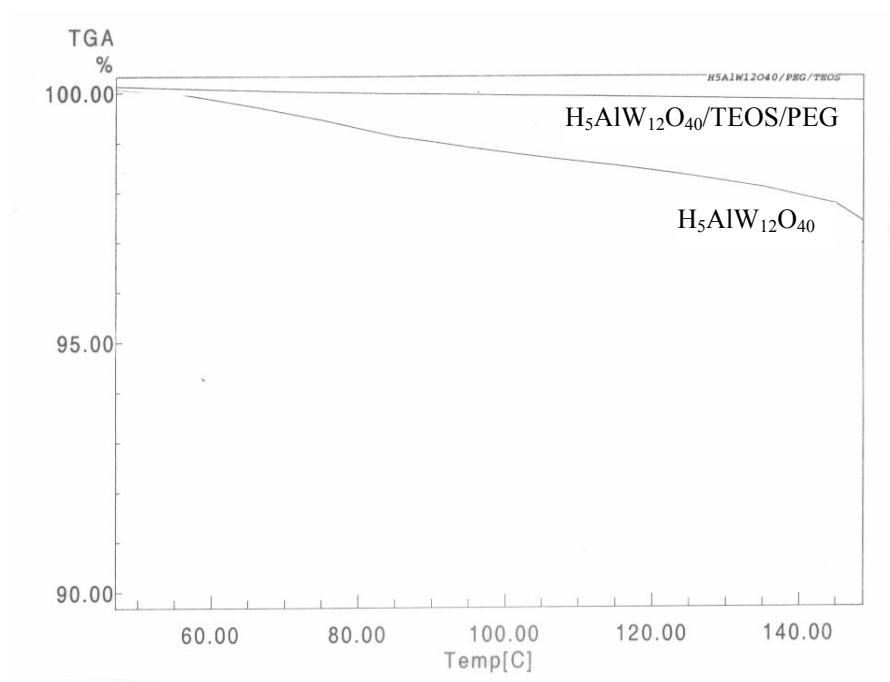


Fig.10 Isothermal TGA of $H_5AlW_{12}O_{40}$ and its hybrid

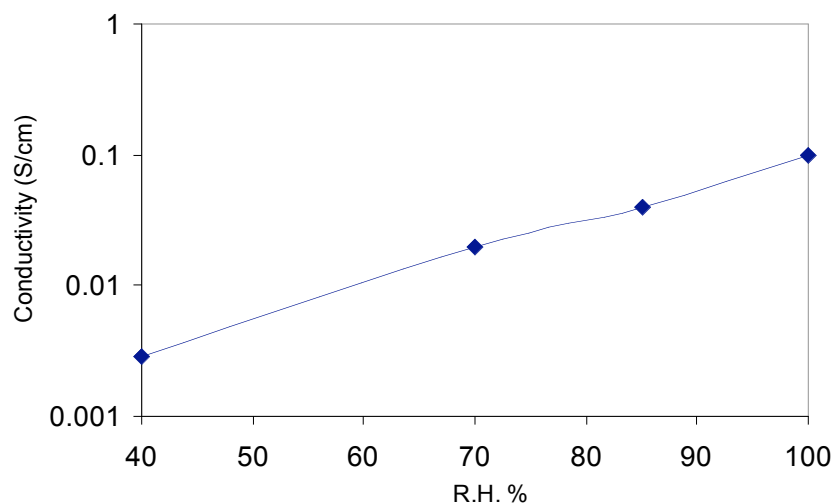


Fig. 11. Relative humidity dependence of conductivity for functionalized PWA at 100°C.

The conductivity was still dependent on relative humidity, as shown in Fig. 11. However, from the slope of the chart, it is not difficult to conclude that this film is much less sensitive to humidity compared to a PWA cluster solid acid pellet.

The proton conductivity of the polyaluminatic acid hybrid and the PWA hybrids at 150°C, and at saturated humidity (20%RH), were compared in Fig. 12. A conductivity of 7×10^{-3} S/cm was obtained in polyaluminatic acid/silica hybrid system (mole ratio of

Al:Si=1:3). The coatings were very stable at 150°C. No significant change in conductivity occurred after three days at 150°C.

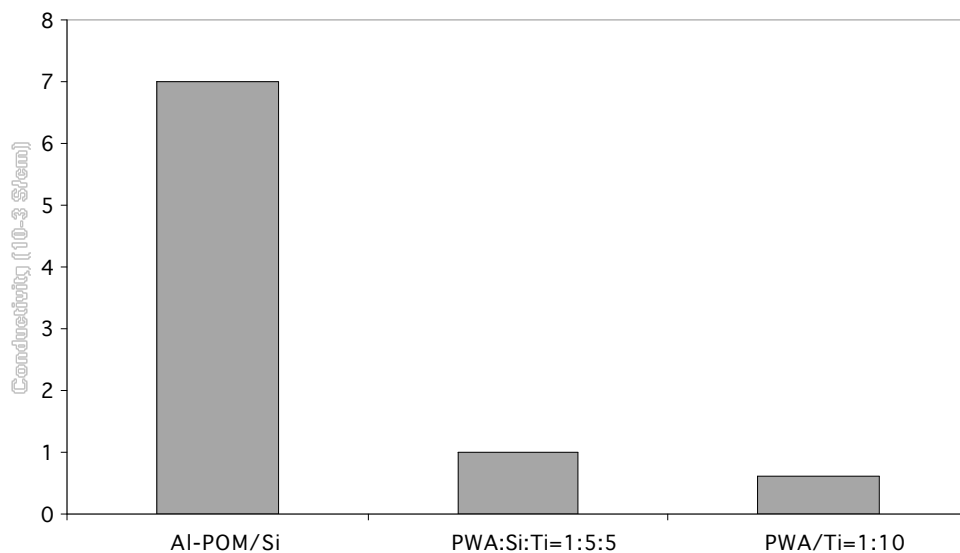


Fig. 12. Proton conductivity of Solid electrolytes at 150°C, 20% RH.

3.7. Fabricate Electrode/electrolyte assembly and Testing

The carbon cloth based electrode was purchased from E-Tek. The electrode was modified with electrolyte solution. The electrode/electrolyte assembly was fabricated by pressing cathode/electrolyte/anode to form a six-inch disk, as shown in Fig. 13.



Fig. 13. Electrode/electrolyte assembly

The cell performance was tested in Fuel Cell Energy. The resistance of the cell was 14.7 mΩ at room temperature and 16.5 mΩ at 80°C. The open circuit voltage was 586 mV at 80°C.

IV. Conclusions and Recommendations

All the project objectives have been successfully accomplished. The proof of feasibility of using polyoxometatate (POM) hybrid membrane-electrolyte assembly (MEA) as high temperature (150°C) proton exchange fuel cell (PEMFC) applications has been firmly established. Furthermore, the testing results show that it has superior high temperature proton conductivity and electrochemical stability over Nafion and other solid electrolytes. This is a key milestone in developing a low-cost, easy-to-manufacturing MEAs for high temperature PEMFC. Due to the successful completion of the research, a solid foundation has been prepared for the future work.

The efforts recommended in the future work include: 1). Further development of high protonic conductive hybrid solid electrolyte by optimization of composition and process parameters; 2) Incorporation of hybrid POM/sol-gel into the cathode to promote intimate contact among Pt, the protonic species and the reactants for high cathode voltage generation; 3) Further development and scaling up of MEAs fabrication technology; 4). Study/testing the MEAs in single fuel cell and optimize the performance of the MEAs.

After successful completion of next phase work, the process will be ready for use in commercial stacks.

Further Development and scale-up the synthesis of Polyaluminatic acid hybrid

In this period of research, we have proven that polyaluminatic solid acid, $H_5AlW_{12}O_{40}$, has much higher protonic conductivity and functionality. This cluster is not commercially available. In this research, we were able to synthesize small amounts of polyaluminatic solid acid. In the future, we need to further develop the synthesis procedure to improve the yield, reproducibility and production capability.

1) Scale-up Production of Polyaluminatic Acid Cluster

In this task, production scale will be increased from <1kg/batch to 20-40 kg/batch. A 50 Liter pilot-scale reactor and extraction set-up will be used to produce large quantities of polyaluminatic acid cluster. All manufacturing conditions will be investigated in detail in order to prepare for subsequent commercial production.

2) Product Development of Solid Acid/Sol-gel Hybrid Electrolyte Precursors

The Polyaluminatic acid/silica gel system showed great potential for the fabrication of a proton exchange membrane. Due to its high proton conductivity, this system material can also be used as proton conductive species in a composite electrode, especially the cathode. In future, we will further develop solid acid/sol-gel hybrid electrolyte precursors.

3) Optimization of the composition and formulation

In next phase, we will focus on AWA solid acid cluster due to its superior conductivity and functionality. It was found that silicate and aluminatic POM are stable to wide range of pH, especially to high pH value. Systemic studies of the effects of

formulation on final electrochemical properties and mechanic properties will be conducted in future.

4) Modification of the solution for composite electrode

It has been found that only 10 to 20% of the platinum catalyst is electrochemically active in the fuel cell reaction. To function, the catalyst must have access to the gas and must be in contact with both the electrical and protonic conductors. In future, we will start with E-Tek's carbon cloth supported Pt/C electrode sheet. The electrolyte coating solution will be adjusted to be carbon wettable and partially wettable to Pt powder. Therefore, when the electrolyte is coated on the electrode, the solution will penetrate into electrode and coat onto the carbon particles, but not the whole Pt powders. Therefore, the Pt will have intimate contact to protonic and electrical conductor and reactants gas.

5) Scale up the production of Hybrid precursors for protonic conductive material

After developing stabilized formulation, production scale will be increased to 30-50 kg/batch. A 50 Liter pilot-scale reactor will be used to produce large quantities of membrane electrolyte precursors. All manufacturing conditions will be investigated in detail in order to prepare for subsequent commercial production.

Product development of high temperature Membrane-electrode assembly

1) Composite electrode

In future, we will use AlWA/sol-gel materials developed in this period as the proton conductor in composite electrode. We will use E-Tek Pt/C particle/C cloth sheet as the starting electrode, and coat a layer of AlWA/sol-gel materials on the surface of the carbon particle by controlling the wettability of the solution to wet carbon, but not Pt (or to only partially wet Pt). The catalyst, Pt, has good contact to the electrical conductor-carbon particle. A continuous electrolyte coating on the carbon particle around Pt will provide an intimate contact between Pt and protonic conductor. Due to the high proton conductivity and high stability of the Chemat electrolyte, the voltage drop due to the electrode will be greatly reduced.

2) Cathode/membrane and Anode/membrane assembly

A technique for the deposition of a dense membrane coating on to composite electrode, with a carbon cloth as the support, will be developed in future. This coating can be applied via spin-coat, spray-coat and dip-coat, as well as screen printing.

In this research, a relatively high protonic conductivity of 7×10^{-3} S/cm was obtained at 150°C and 20% of R.H. at ambient pressure in the three-month development period. This is among the best results for the solid electrolyte in PEMFC. The proton conductivity can be greatly increased by increasing the humidity (in pressurized fuel cell). Based on the results and data collected in this research, we will develop MEAs with a thickness of 30-100 μm for ambient pressure application and 60-300 μm for pressurized fuel cell application.

3) Cathode/membrane/anode assembly

The procured cathode/membrane and anode membrane are pressed together and form good contact by further higher temperature curing.

Evaluation of MEAs in Fuel cell

The promising MEAs will be tested in fuel cell with three surface areas: 25, 50 and 300 cm². The MEAs will be evaluated in hydrogen-air and reformat-air fuel cell. All the data will be collected and used for fuel cell design. FuelCell Energy, will be our first customer. FCE has been successfully conducted a 2 MW size field test for more than 5 years. They are currently developing PEMFC. Therefore, Chemat's novel MEAs can be incorporated into their PEMFC for field test.

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